



Direct construction of diverse metallophthalocyanines by manifold substrates in a deep eutectic solvent



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ABSTRACT

Direct access to a wide range of metal-free phthalocyanines and metallophthalocyanines in deep eutectic solvents (DESs), is reported. Substituted and unsubstituted phthalocyanines of Mn, Fe, Co, Ni, Cu, Zn, Pd, In, and Pt with various raw materials such as phthalonitriles, phthalimides, phthalic anhydrides and phthalic acids are successfully prepared in the DES based on choline chloride and urea in a very short reaction time with appropriate yields. It has been shown that DES as a green and rapidly degraded reaction medium in the environment plays a triple role as a solvent, organocatalyst, and reactant in this process. Moreover, the DES system could be separated and reused in four consecutive reaction runs with no considerable loss in catalytic activity.

1. Introduction

Phthalocyanines constitute a very important class of compounds with many technological applications [1]. Metallophthalocyanines and their derivatives are intensively used as dyes [2], photosensitizer agents [3], optical materials [4], solar cells [5], fluorescence “off-on-off” sensor [6], photodynamic therapy [7] and electrical properties [8] also as a catalyst in chemical engineering transformation processes [9,10] and organic reactions [11–13]. Notably, the most important feature which makes these molecules play a remarkable role in the area of material science is their versatility and their chemical and thermal stability. The two hydrogen atoms of the central cavity in metal-free phthalocyanines can be replaced by more than 70 central metals and a diverse kind of substituents can be incorporated, thus giving attractive properties to these molecules [14]. Intensely colored metal complexes of phthalocyanines make them a great candidate for manufacturing dyes and pigments. The worldwide production of metallophthalocyanines is about 80,000 tones valued over one billion U.S. dollars. The usage of colorants is about 40% for printing inks, 30% for varnish or paints, 20% for coloring plastics and 10% for other finishes [15]. On the other hand, 25% of synthetic organic pigments are phthalocyanines and their derivatives [16].

Typically, metallophthalocyanines are prepared by cyclotramerization of phthalonitriles or phthalic acid analogues such as phthalimides, phthalic anhydride and phthalic acid at high temperatures

around 200 °C and reaction times of several hours are needed (10–24 h). For example, phthalocyanines were prepared from phthalonitrile derivatives in DMF [17] at 150 °C and pentanol [18] at 160 °C. In the case of phthalimide derivatives, the reaction carried on at the higher temperature (200 °C) and longer reaction times [19]. When phthalic anhydrides were used as substrates more high temperature needed (220 °C) [20]. In addition, toxic solvents, for example, dichlorobenzene [21], nitrobenzene [22] and quinoline [23] were usually used in these processes. Moreover, the utilization of strong bases and expensive additives such as 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) [24], hexamethyldisilazane (HMDS) [25], ionic liquids [26], cerium(III) chloride [27] or particularly microwave irradiation conditions [28,29] are common for the synthesis of phthalocyanines. These methods have some drawbacks regarding to their harsh reaction conditions, utilizing toxic metals and solvents, expensive strong bases, non-reusability, increasing of waste as an undesirable factor in green chemistry and the need for special apparatus such as microwave. The increasing importance and application of phthalocyanines as advanced materials have created an impetus for designing the sustainable and facile synthesis medium to reach these high-performance compounds.

Deep eutectic solvents (DESs) as an efficient and neoteric media have gained widespread attention in the last decade. Subsequently, DESs are formed by combination of the tertiary ammonium chloride known as choline chloride and a series of hydrogen bond donors (HBD), for example, urea, sugars, carboxylic acids and glycerol [30,31].

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DESs have similar features, but considerable advantages over ionic liquids (ILs), such as being biodegradable and non-toxic starting materials, cheaper production process and lower cost of the raw materials and importantly it can be sourced from renewable feed stocks and rapidly degraded in the environment [32]. Some advantages of DESs compared to molecular solvents are non-volatility, inflammability and a wider liquid temperature range [33]. Nowadays, DESs have been applied in different chemical processes such as extraction [34], polymerization [35], electrochromic devices [36], carbon dioxide capture [37], and they act as an efficient medium for synthesis of nanoscale and functional materials [38] besides various organic and inorganic transformation [39,40].

2. Results and discussion

As part of our continued interest in developing new methods for the synthesis of various phthalocyanines [41,42] and their applications [43–45] as well as using deep eutectic solvents as green medium for organic transformations [46–49], herein, we describe the clean synthesis of metal-free phthalocyanines and metallophthalocyanines from various raw materials such as phthalonitriles, phthalimides, phthalic anhydrides and phthalic acids in the DES based on choline chloride and urea in a very short reaction time with appropriate yields. To the best of our knowledge, this is the first investigation on the synthesis of phthalocyanines in DESs and these new reaction media open an important alternative to utilizing volatile organic solvents and ionic liquids. This synthetic strategy involves a green and eco-compatible approach for the quick synthesis of phthalocyanines at low temperature in high purity and offers an easy workup procedure without any additives (Scheme 1).

In the beginning, in order to determine the best deep eutectic solvent, we studied the reaction of phthalonitrile **1a** and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

Table 1

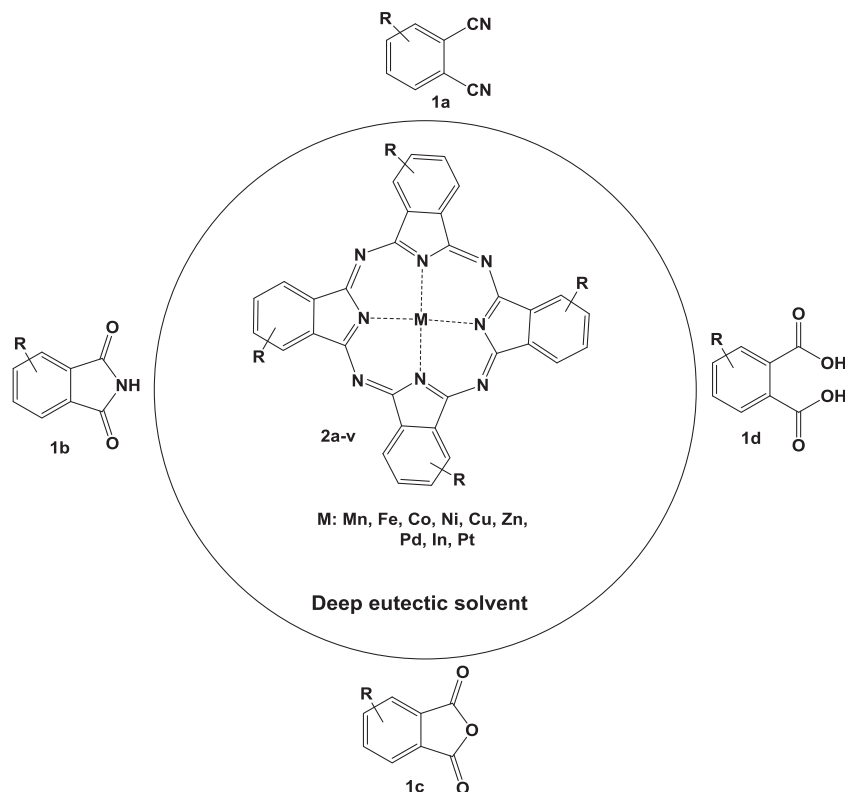
Optimization of conditions for the synthesis of copper phthalocyanine **2a**^a in various deep eutectic systems.

Entry	DES (Molar ratio)	Temperature (°C)	Time (min)	Yield (%) ^b
1	Choline chloride: urea (1:2)	120	15	75
2	Choline chloride: urea (1:2)	140	5	72
3	Choline chloride: urea (1:3)	120	15	75
4	Choline chloride: urea (1:4)	120	15	35
5	Choline chloride: PTSA (1:1)	120	15	0
6	Choline chloride: ethylene glycol (1:2)	120	15	Trace
7	Choline chloride: glycerol (1:2)	120	15	0
8	Choline chloride: oxalic acid (1:2)	120	15	0
9	Guanidinium chloride: urea (1:2)	120	15	0
10	Choline chloride: urea (1:2)	r.t.	60 to 600	0
11	Choline chloride: urea (1:2)	80	15	0
12	Choline chloride: urea (1:2)	80	600	Trace
13	Choline chloride: urea (1:2)	80	1800	30
14	Choline chloride	120	15	0
15	Urea	120	15	25
16	DES free	120	15	0

^a Reaction conditions: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (42.620 g, 0.250 mmol), phthalonitrile (0.128 g, 1.000 mmol).

^b Isolated yields.

as a model reaction in various DES systems based on the choline chloride with hydrogen-bond donors such as urea, ethylene glycol, PTSA, glycerol and oxalic acid at different temperatures and reaction times (Table 1). The results were not successful in all of the hydrogen-



Scheme 1. Synthesis of phthalocyanines using diverse raw materials in a deep eutectic solvent.

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